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13. ABSTRACT *(Maximum 200 words)* The objective of this Phase II Small Business Innovation Research project was to develop an efficient and cost-effective biological process to treat air emissions of significance to the Navy. During Phase I, the feasibility of treating these emissions using a *biotrickling filter* was tested. Biotrickling filters are similar to chemical scrubbers, but rely on microorganisms on the packing surface to remove and oxidize contaminants rather than chemicals. A 7-month field-pilot demonstration was conducted at North Island Naval Air Station near San Diego, California to demonstrate the effectiveness of the process for treatment of hazardous air pollutants (HAPs) from spray paint booths. Target HAP removals exceeded 88 percent for vapor contact times (packing volume divided by air flowrate) greater than 16 seconds. Carbon dioxide measurements indicated that the dominant removal mechanisms were absorption and biodegradation in the morning hours and biodegradation only in the afternoon hours. Performance was not affected by the intermittent operation in the paint booth. A cost analysis showed that for treatment of the entire air stream, over a 10-year project life, biotrickling filters designed for a 16 or 11 second contact time were less expensive than carbon adsorption or thermal systems.

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FINAL REPORT

Grant #: N00014-96-C-0370

PRINCIPAL INVESTIGATOR: A. Paul Togna, Ph.D.

INSTITUTION: Envirogen, Inc.

GRANT TITLE: Development of Biotrickling Filters to Treat Sulfur and VOC Emissions

AWARD PERIOD: 30 September 1996 - 29 September 1998

OBJECTIVE: The objective of this Phase II SBIR project was to develop an efficient and cost-effective biological process to treat air emissions of significance to the Navy, including sulfur-containing gases, noxious odors, volatile organic compound (VOC) emissions, and hazardous air pollutants (HAPs).

APPROACH: During Phase I, the feasibility of treating these emissions using a second generation fixed-film bioreactor design, a *biotrickling filter*, was tested. Biotrickling filters are similar to chemical scrubbers, but rely on microorganisms on the packing surface to remove and oxidize contaminants rather than chemicals.

The Phase II project involved laboratory-scale, transition-scale, and field-pilot experiments. Biofilm stability, operating range, and mass balance tests were conducted using laboratory-scale biotrickling filter columns of approximately 100 and 150 mm (4 and 6 inches) in diameter. Media pressure drop experiments were conducted using a larger transition-scale biotrickling filter column of approximately 330 mm (13 inches) in diameter. The field-pilot demonstration was conducted using a pilot-scale system consisting of a biotrickling filter column of approximately 70 cm (24 inches) in diameter.

Toluene, xylenes, methyl ethyl ketone (MEK), and n-butyl acetate were chosen as the VOC/HAP target contaminants for the laboratory studies. Hydrogen sulfide (H_2S) and methyl mercaptan were chosen as representative odor targets.

An operational biomass growth control mechanism was investigated based on nutrient (potassium) limitations and establishment of a "biological equilibrium." Two sets of laboratory-scale columns were operated: (1) an experimental set; and (2) a control set. Activated sludge was added to the experimental columns to promote predation, and potassium levels were kept low. The control columns received no sludge and had high potassium levels. The effects of intermittent contaminant loading on biofilm stability were also investigated. The laboratory-scale columns were operated under varying influent contaminant concentrations, vapor flowrates, and liquid re-circulation rates in order to obtain the preliminary operating range of these systems for both paint booth and odor applications. Mass balances around the systems were performed in order to assess the degree of contaminant conversion to CO_2, biomass, and SO_4^{-2} (for odor applications).

During transition-scale experiments, the pressure drop across the packing material showing the best overall performance during the laboratory tests was evaluated under flowrate conditions expected during full-scale system operation, with actively growing biomass on the media. The growth substrate for the biomass was ethanol.

A 7-month field-pilot demonstration was conducted at North Island Naval Air Station (NAS) near San Diego, California to demonstrate the effectiveness of the biotrickling filter process for treatment of VOCs and HAPs from spray paint booths.

ACCOMPLISHMENTS: During the 6-week laboratory-scale intermittent loading experiment, no noticeable increase in pressure drop across any of the columns was observed. Under continuous loading conditions, the pressure drops through all the columns were higher and less stable than those observed during intermittent loading.

Throughout the continuous loading experiments, potassium concentrations in the re-circulating water within the experimental columns (which also received activated sludge) were maintained at low levels (target less than 10 mg/L). There was no evidence that potassium limitations or addition of activated sludge minimized biomass growth. Greater than 80 percent contaminant conversion to CO_2 was observed for all systems, and close to 100 percent conversion was observed a majority of the time. However, contrary to published reports, low potassium levels reduced performance (removal efficiency).

The operating range experiments showed that biotrickling filters are most effective at degrading VOCs at low concentrations and high contact times (media volume divided by vapor flowrate). The tests also showed that high removal efficiencies require controlling biomes growth which, if left unchecked, caused plugging, decreased effective vapor residence time, and clogged the liquid re-circulation pump and lines. A low liquid re-circulation rate combined with high vapor velocity had a significant adverse impact on perfomance. High vapor flow had a substantial drying effect on the biomass. MEK and n-butyl acetate were degraded with close to 100 percent efficiency during nearly all operating conditions tested. The aromatic hydrocarbons toluene and xylenes were removed with less efficiency, and were less likely to be degraded under less favorable conditions such as low contact time, high loading, and low nutrient (potassium) concentrations.

For the odor experiments, H_2S and methyl mercaptan were degraded with close to 100 percent efficiency. Visually, there was no increase in the amount of biofilm on the packing over the length of the experiments and no significant pressure drop increase was observed.

Under low loading conditions, near-complete contaminant conversion to CO_2 was observed when the systems reached equilibrium. At higher loading conditions, CO_2 concentrations began to lag behind the level of

VOCs degraded, leaving an unaccounted portion of carbon, likely directed toward biomass accumulation.

At low sulfur loading, nearly all of the sulfur in the effluent was in the form of SO_4^{2-} in the discharge liquid. A delay in the increase of sulfate in the discharge liquid was observed after the contaminant concentration in the influent vapor was increased. It is likely that during these transient periods of increased sulfur load, incomplete oxidation of sulfide to sulfur, rather than sulfate, was occurring. Caustic usage declined during these same periods.

The results of the transition-scale experiments showed that a maximum pressure drop of less than 0.5 " H_2O per foot of media can be expected when operating and designing full-scale systems.

During the field-pilot demonstration, total VOC removals ranged from 70 to 85 percent, while individual target compound removals varied. Generally, MEK, methyl isobutyl ketone (MIBK), and n-butyl acetate were removed with close to 100 percent efficiency. The aromatic compounds were removed with lower efficiency (0 to 96 percent), but constituted only a small fraction of the total HAPs. Target HAP removals exceeded 88 percent for contact times greater than 16 seconds. CO_2 measurements indicated that the dominant VOC removal mechanisms were absorption and biodegradation in the morning hours, and biodegradation only in the afternoon hours. Performance was not affected by the intermittent operation in the paint booth. Although air from the paint booths was constantly supplied to the system, contaminants were present in the air for only 6 to 8 hours each day for 4 to 5 days each week, when painting was occurring. A downtime that lasted greater than two weeks did not significantly hamper system performance once operations were resumed.

Using the results of the field-pilot demonstration, a cost analysis was performed to assess treatment of the total paint booth emissions. The design flowrate was 12,600 cubic feet per minute. The cost analysis showed that for this application, over a 10-year project life, the least expensive treatment technology is a biotrickling filter designed for a 16 or 11 second contact time. The next least expensive technology is carbon adsorption. On the basis of cost per ton of HAP treated, biotrickling filters and carbon adsorption have approximately the same net present cost (NPC), assuming a 10-year project life, an interest/inflation rate of 4 percent and a discount rate of 12 percent. Thermal technologies (catalytic and regenerative) have NPCs approximately 10 to 40 percent higher. The predicted HAP removal efficiencies for the biotrickling filters range from 80 to 90 percent. The predicted HAP removal efficiencies for the carbon adsorption and thermal technologies range from 95 to 99 percent. However, significant quantities of natural gas are required for the thermal technologies, and therefore significant amounts of CO_2 are produced. For carbon adsorption, the ketones in the feed stream (MEK and MIBK) create a self-ignition and explosion hazard.

<u>CONCLUSIONS</u>: Based on the laboratory results, it appears that biomass growth within biotrickling filters can be controlled effectively if the

contaminant supply is intermittent, provided the contaminant loads are similar to those used during the laboratory experiments and observed during the field-pilot demonstration. During the laboratory tests, the effects of activated sludge addition and potassium limitations on biomass growth were either not significant under the conditions tested, or were masked by the intermittent contaminant feed. However, low potassium levels significantly reduced performance. Under moderate loading, mass balances showed that the contaminants were transformed primarily into CO_2 and SO_4^{-2} (when treating reduced sulfur compounds). Under high loading conditions, more of the contaminant carbon appeared to be directed toward biomass growth, and incomplete oxidation of sulfide to sulfur appeared to occur. The results of a cost and technical analysis show that for spray paint booth applications, biotrickling filters offer significant cost and safety advantages compared to conventional carbon adsorption and thermal technologies.

SINGNIFICANCE: Based on the successful project results and favorable economic evaluation, the Navy should consider the use of biotrickling filters for treatment of spray paint booth and other point source emissions. Prior to the completion of this Phase IIa Final Report (Base Case), ENVIROGEN received a Phase IIb (Option) contract (N00014-99-C-0036) to supply the Navy Public Works Center with a biotrickling filter to treat 3,000 cfm of air from four of the wastewater holding tanks at the Industrial Water Treatment Plant at NAS North Island.

PATENT INFORMATION: None

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PUBLICATIONS AND ABSTRACTS (for total period of grant):

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2. Webster, T.S., A.P. Togna, Y. Yang, and W.J. Guarini. From Bench- to Pilot-Scale Experimentation: The Treatment of Volatile Organic Compound Emissions from Spray Paint Booth Applications Using a Biological Trickling Filtration Reactor. Paper No. 98-MP20A.04. 91st Annual Air & Waste Management Association Meeting and Exhibition in San Diego, California, June 14-18, 1998.

3. Webster, T.S., A.P. Togna, W.J. Guarini, and L. McKnight. Treatment of Volatile Organic Compound Emissions for a Spray Paint Booth Application using Biological Trickling Filtration. Proceedings of the 1998 USC-TRG Conference on Biofiltration, University of Southern California, Los Angeles, California, October 22-23, 1998, pp. 41-50.

4. Webster, T.S., A.P. Togna, W.J. Guarini, and L. McKnight. Application of a Biological Trickling Filter Reactor to Treat Volatile Organic Compound Emissions froma Spray Paint Booth Operation. *Metal Finishing*, March 1999, pp. 20-26.